

# A Crystalline Polymer Morphologist's Perspective on the Occasion of the Centenary of the Foundation of the American Physical Society

F. KHOURY

NIST

Mailing address: Polymers Division, NIST, Gaithersburg, Maryland 20899

The centenary celebration of the American Physical Society in 1999 will correspond to the 55th anniversary of the Society's Division of High Polymer Physics (DHPP) whose inaugural meeting was held in Rochester, NY on June 23 and 24, 1944. I attended my first DHPP meeting in March 1958 shortly after emigrating to the U.S., my third and last continental home, having grown up in Alexandria, Egypt, and then pursued my undergraduate and graduate studies at the University of Leeds (1949–1956) in the U.K., followed by an early industrial R&D experience at British Nylon Spinners (BNS) in Pontypool, Monmouthshire. It is, upon joining the research laboratories of the latter company early in 1956, that I was pointed to the crystallization and morphology of synthetic polymers and started along the path of what was to become a career-long interest in determining the nature, and elucidating the origins, of the diversity in the crystallization habits exhibited by polymers when crystallized under quiescent conditions, particularly, but not exclusively, from solution. That my endeavors in the area of the morphology of crystalline polymers started in an industrial research laboratory is a common factor among many of my contemporaries and elders in this field.

In the U.S., I pursued my interest in the fundamentals of polymer morphology with varying intensity as opportunity offered over the years, first in industry (at FRL Inc. Dedham, MA, then at the American Viscose Corporation/Avisun Corporation, Marcus Hook, PA), and subsequently from June 1963 up to my retirement in October 1992, in the Polymers Division of the National Bureau of Standards/National Institute of Standards and Technology. I hold a particular affection for the Annual March Meetings of the DHPP all of which I have attended, with one exception, since 1958, and at which I have presented con-

tributed and invited papers. The conviviality that developed over the years among the regular attendees with common research interests at these meetings has been most pleasurable.

I started (1956) my post-PhD research career at BNS new to spherulitic crystallization in synthetic polymers and at the immediate predawn of the "lamellar" era of polymer crystallization and morphology. This era, which was heralded convincingly by the three well-known papers published in 1957 by A. Keller, E. W. Fisher, and P. H. Till, Jr., respectively, corresponded also with a time when stereoregular polymers were becoming more broadly available for study. These two factors coupled with the perfecting and proliferation of the electron microscope as a research tool by the mid-1950s led to a veritable explosion in the study of the morphology of crystallizable polymers; it has been my good fortune to be a participant.

Bracketed between my earliest studies on the morphology of nylon 66 spherulites,<sup>1</sup> and latest work (as a collaborator of Dr. Robert Briber) concerning as yet to be fully resolved complexities of the development of banded polymer spherulites in the case of poly(vinylidene fluoride) crystallized from blends with poly(ethyl acrylate),<sup>2</sup> are investigations of various aspects of the crystallization habits of other polymers including several polyolefins, poly(oxymethylene), poly(chlorotrifluoroethylene), and a paraffin (C<sub>94</sub>H<sub>190</sub>). I will confine my remarks in this note to the detailed study of the morphology of isotactic polypropylene crystallized in the  $\alpha$ -monoclinic form which I published many years ago<sup>3</sup> and also presented in parts at DHPP meetings in March 1963–1965. The paper<sup>3</sup> is entitled "The Spherulitic Crystallization of Isotactic Polypropylene from Solution: On the Evolution of Monoclinic Spherulites from Dendritic Chain-Folded Crystal Precursors." I think it is fair to say that this work served as a useful benchmark for subsequent studies of many others aimed at elucidating the origins of exceptional crystallization habits and morphological characteristics exhibited by  $\alpha$ -polypropylene when crystallized from solution and from the molten state. As indicated in the introduction of that paper,<sup>3</sup> I was aware at the outset of the work of brief reports of an unusual and ill-understood cross-hatched morphology seen in electron micrographs of melt crystallized polypropylene, but delving into this phenomenon was not the initial objective of the work. Paralleling the then voluminous on-

going studies of polyethylene crystals, my initial intention was to grow, in suspension, lamellar single crystals of polypropylene from solution and to determine the lateral growth habits of the lamellae and their conformations. This endeavor, which involved probing the use of different solvents, polymer concentrations, and temperatures, was not successful. During this exploratory work, however, conditions were established in which polypropylene spherulites were grown reproducibly from solutions of the polymer in xylene as well as in mineral oil. Briefly, the nonvolatile nature of the latter solvent proved to be a great boon. It allowed the easy observation of the growth of the spherulites from solution under isothermal conditions using a simple hot stage set-up under a light microscope using phase contrast optics. This facility led to the detection and characterization of the progressive evolution of  $\alpha$ -spherulites from their very earliest stages of growth which were characterized by the formation of precursor objects exhibiting a rectangular (nearly square, a few micrometers on a side) overall shape, and which, it could be surmised from their appearance from different perspectives, were thinner than long or broad (e.g., see Fig. 14 in Ref. 3). Given their transient nature, these precursor structures were not amenable to easy isolation and detailed morphological examination. Further experiments, using amyl acetate as a solvent, resulted in the crystallization of the polymer entirely in the form of such precursor structures as end products in suspension. Accordingly, they could be readily isolated and studied in detail using electron microscopy and electron diffraction. The results are well established.

Recapitulating briefly, the overall shape of these objects approximated that of a rectangular parallelepiped (Cartesian coordinates  $x$ ,  $y$ ,  $z$ , where  $x/y \approx 1.1$ , and  $y > 2z$ ). The surprising fact was that these objects exhibited a distinctive cross-hatched fine structure when viewed in the  $z$ -direction. They consisted of a dense network of two intercrossing families of monolayer chain-folded lamellar branches which traversed the object parallel to one or the other diagonal directions with respect to the  $x$ ,  $y$  cross-section, and with their fold surfaces (considered to be (001)), as well as the  $b$ -axis, at right angles to that cross-section. The preferential growth axis of the lamellae was the  $a$ -axis which was oriented parallel to the corresponding diagonal direction. The angle between the respective orientations of the  $c$ -axis

in the one set of diagonally oriented lamellar branches relative to the other was close to  $80^\circ$ . The implication was that the evolution of these objects, now commonly referred to as "quadrites" (a term I originally coined but did not use in the paper),<sup>3</sup> involved  $80^\circ$  changes in orientation of the chain axis ( $c$ -axis) in offspring lamellar branches relative to their parent branches. This feature, which is at the root of the cross-hatched morphologies exhibited by polypropylene crystallized in the  $\alpha$  (monoclinic) form, represented a departure from the then generally encountered compliance of the habits and mechanisms of growth of polymer single and twinned lamellar chain-folded crystals, which exhibited the inherently characteristic parallel mode of chain packing which long chain compounds adopt in the crystalline state. Homoepitaxy as the root cause of the branching strongly suggested itself. My speculation that it might originate at the fold-surfaces was however not borne out. Subsequently published investigations, in particular by Padden and Keith,<sup>4</sup> and Binsbergen and de Lange,<sup>5</sup> indicated that branching is a consequence of the homoepitaxy of daughter lamellae on the lateral (010) faces of parent lamellae. These studies coupled with findings due to Lovinger,<sup>6</sup> led in turn to the rigorous analysis and accounting of the mechanism of branching which governs the evolution of quadrites by Lotz and Wittman in a paper<sup>7</sup> published in 1984 entitled "The Molecular Origin of Lamellar Branching in the  $\alpha$  (Monoclinic) Form of Isotactic Polypropylene." The formation of quadrites is summarized in a more general context in an extensive review by Bruckner, Meille, Petraconne, and Pirozzi entitled "Polymorphism in Isotactic Polypropylene."<sup>8</sup>

## REFERENCES AND NOTES

1. Khoury, F. *J Polym Sci* 1957, 26, 375; idem 1958, 33, 389.
2. Briber, R. M.; Khoury, F. *J Polym Sci, Part B: Polym Phys* 1993, 31, 1253.
3. Khoury, F. *J Res Nat Bur Stds (U.S.)* 1966, 70A, 29.
4. Padden, F. J.; Keith, H. D. *J Appl Phys* 1966, 37, 4013.
5. Binsbergen, F. L.; deLange, B. M. G. *Polymer* 1968, 9, 23.
6. Lovinger, A. J. *J Polym Sci, Polym Phys Ed* 1983, 21, 97.
7. Lotz, B.; Wittman, J. C. *J Polym Sci, Part B: Polym Phys* 1986, 24, 1541.